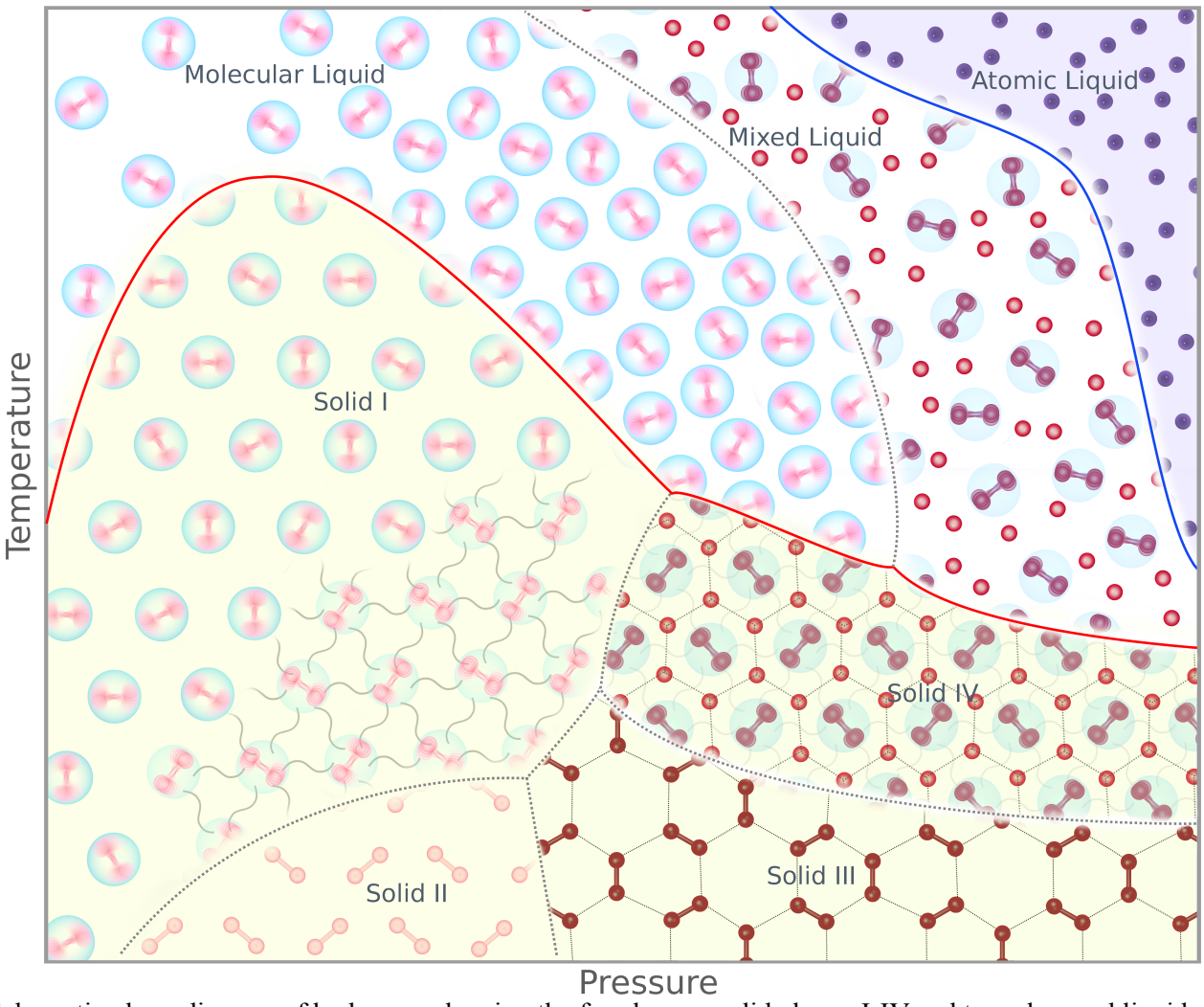
Bearing down on hydrogen



Schematic phase diagram of hydrogen, showing the four known solid phases I-IV and two observed liquid phases, together with predicted atomic liquid. Blue rings imply rotating quantum molecules, wiggly lines imply entangled rotor state, solid “bonds” are where calculation shows a covalent bond.

Abstract

Under high pressure, the electrons can be squeezed out of the covalent bond which holds the hydrogen molecule together. Under these conditions, condensed hydrogen can become metallic, but the pressures required can be obtained only through the gravitational field of gas giant plants, or fleetingly in shock waves. Elsewhere in this issue, Knudson et al[1] report experiments using the Sandia Z-machine, which uses giant electric pulses to generate concentrated shock waves in a tiny sample[2]. They observe metallic liquid hydrogen created for a tenth of a microsecond at the shock wavefront.

It took 50 years from prediction to discovery of the Higgs boson, but 80 years on the most famous conjecture in condensed matter physics remains unproven. In 1935, 24-year old PhD student Hillard Huntingdon and his supervisor Eugene Wigner calculated the properties of metallic hydrogen[3]. Based on a nearly-free electron picture they calculated that simple atomic structure such as bcc would be some tenfold denser than cold molecular hydrogen. Ignorant of the compressibility, they stated that the required pressures would be ``above 35GPa'': a seemingly impossible pressure in those days.

The conversion was unfortunate: it turned out that the compressibility of hydrogen is much lower than they guessed, and to reach the required density, a pressure more like 350GPa is required and their 35GPa value is still frequently ridiculed. They also underestimated the ingenuity of experimentalists, as such ``impossible'' pressures are now obtained by two separate methods: shock compression and diamond anvils.

The assumption was that at high pressures hydrogen would become like the other Group I elements. When sufficient mechanical energy is applied to overcome the binding energy of the electron in the covalent bond, hydrogen could free electron like and would transition from molecular-insulator to atomic metal. This picture of hydrogen as a group I element is now confounded by the discovery that when such pressures are applied to simple metals, their electronic structure transforms *from f*ree electron metal to insulating ``electrides'', where valence electrons move away from the nuclei to interstitial ``pseudoanion'' sites[4]. Moreover, just as the idea that atomic structures need not be metallic was taking hold, calculations on hydrogen started predicting that some molecular structures may be metallic[5].

Adding to this conceptual confusion is the fact that the hydrogen atom is light enough that the thermal de Broglie wavelength approaches the interatomic spacing. Under these conditions, the nuclei must be treated as indistinguishable quantum particles, which has led to the prediction of various exotic phases of matter such as superfluids, or superconductors based on either proton or electron Cooper pairs[6]. Under such conditions the behaviour of deuterium (as used by Knudson), would be radically different, due to its higher mass and bosonic nucleus.

At high temperatures the difference between deuterium and hydrogen is likely to be less important. Traditional shock experiments can only traverse a particular set of isentropic P,T states: the ``Hugoniot'', and these are different for hydrogen and deuterium. The shaped pulses of the Z-machine enable access to different T isentropes allowing a range of PT space to be explored.

The structure of solid hydrogen to 250GPa is now well established[7]. Phase I is a hexagonal close-packed molecular liquid. Here the high-school image of H_2 as a dumbbell molecule is misleading, at low pressure H_2 behaves as a free rotor, and the J=0 quantum ground state is spherical. Hence phase I can be thought of as simply close packing of spherical molecules. As pressure increases, the molecules interact and J ceases to be a good quantum number. At low temperature this leads to a ``broken symmetry'' Phase II, where the rotation has stopped. At high temperature, the melt line shows a maximum around 900K/70GPa: if pressure is increased further the melting temperature drop, meaning the the liquid is denser than the close-packed crystal[8,9]. Under further pressure, according to theory, a new motif appears - groups of three hydrogen molecules arrange themselves into hexagonal trimers. The electrons are not yet dissociated, and the structure remains non-metallic, but the covalent bonding is much weaker. In the low temperature ``Phase III'' all molecules are in such trimers, however at high temperature ``Phase IV'' appears to comprise alternating layers of trimers and relatively freely rotating molecules. This is found in simulation, and evidenced experimentally by the appearance of two distinct molecular vibration frequencies[10,11]. Curiously, if one treats the trimers as independent atoms, and the free molecules as a spherical unit, the average structure seen in molecular dynamics calculation is that of MgB_2. This is the densest possible packing for binary hard spheres mixtures with comparable radii: the notion that at high pressure hydrogen simply adopts the most efficient packing is compelling.

Although there are many theoretical predictions, no metallic solid phase of hydrogen has yet been produced. Nor is it resolved whether the melting temperature continues to drop to, perhaps to zero in a quantum superfluid, or rises again when metallic phases occur.

Which returns us to the liquid phase. The diagnostic used by Knudsen et al is VISAR - essentially looking for the reflection of visible light from the interface between deuterium sample and it aluminium holder. The first strong signal is the loss of signal around 120GPa: this is not a strucural transition - the bandgap has closed to absorb visible light. Then at 280-300GPa the signal reappears, implying band gap closure which is primarily driven by compression rather than heating. Simulations in these conditions suggest the onset of molecular dissociation, however the calculated metallization pressure depends sensitively on the approximations made in the calculation[1,8,12,13].

Thus it appears that metallization occurs at lower pressures in the liquid than in the solid, where static compressions now exceed 350GPa. But before concluding that the liquid is somehow ``easier'' to metallise we should recall those 80 year-old conversion difficulties. The liquid is denser than the solid, and

the compressibility is not precisely known. The transition density may well be similar.

[1] Knudsen et al. this issue
[2] M. Matzen, et al., Phys. Plasmas 12, 055503 (2005).
[3] Wigner & Huntingdon J. Chem. Phys. 3, 764 (1935).
[4]M. Marques, M. I. McMahon, E. Gregoryanz, M. Hanfland, C. L. Guillaume, C. J. Pickard, G. J. Ackland, and R. J. Nelmes, Physical Review Letters 106, 095502 (2011).
[5] C. J. Pickard and R. J. Needs, Nature Physics 3, 473 (2007).
[6] E. Babaev, A. Sudbo, and N. Ashcroft, Nature (London) 431, 666 (2004).
[7] J. M. McMahon, M. A. Morales, C. Pierleoni, D. M. Ceperley, Rev. Mod. Phys. 84, 1607 (2012).
[8] J Chen, XZ Li, Q Zhang, M I J. Probert, C. J. Pickard, R. J. Needs, A. Michaelides and E. Wang Nature Communications 4, 2064 (2013)
[9] R. T. Howie, P. Dalladay-Simpson, and E. Gregoryanz, Nature Materials 14, 495 (2015).
[10] I. B. Magdau and G. J. Ackland, Physical Review B 87, 174110 (2013).
[11] R T. Howie, C L. Guillaume, T Scheler, A F. Goncharov, and E Gregoryanz Phys. Rev. Lett. 108, 125501 (2012)
[12] I. Tamblyn and A. Bonev, Phys. Rev. Lett. 104, 065702 (2010).
[13] M. A. Morales, C. Pierleoni, E. Schwegler, D. M. Ceperley, Proc. Natl.Acad. Sci. U.S.A. 107, 12799 (2010), Phys. Rev. Lett. 110, 065702 (2013).